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⑦① Applicant: Airwick AG, Postfach, CH-4005 Basel (CH)

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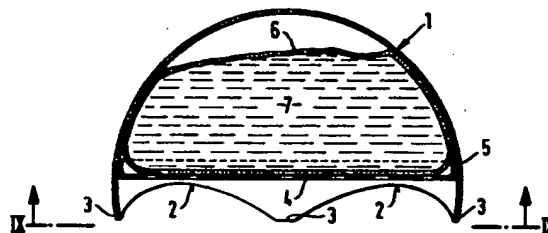
⑦② Inventor: Lee, Ping I., Dr., 38-1/2 Wolden Road,
Ossining New York 10562 (US)
Inventor: Kleiner, Eduard K., 207 East 74th Street, New
York N.Y. 10021 (US)

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⑦④ Representative: Schiner, Rolf et al, Patentabteilung
der CIBA-GEIGY AG Postfach, CH-4002 Basel (CH)

⑤④ Dispensing system for vapors of a volatile odor-controlling material.

⑤⑦ A system for the controlled release of air treating material comprising a hydrophilic membrane forming part of the wall of a reservoir containing an air-treating ingredient in aqueous medium, the membrane serving as the means for releasing vapors of the ingredient and water vapor to the atmosphere and for controlling the rate of release. The release is practically constant, and fractionation of components of the air-treating ingredient and of the latter and water is reduced or practically eliminated.



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Dispensing System for Vapors of a Volatile Odor-Controlling
Material

This invention relates to a dispensing system for vapors of a volatile odor-controlling material comprising a closed reservoir and a membrane forming at least a portion of the wall of the reservoir and having an external surface in contact with the surrounding atmosphere, and an odor-controlling agent-containing liquid in the said reservoir in contact with the internal surface of the membrane.

A dispensing system of this type is described in U.S. patent 3,669,637 of Klass et al. In this known system containers equipped with membranes, for instance of water-soluble cellulosic polymers, polyvinyl alcohol or gelatin are filled with a liquid odorant, e.g. a mercaptan which permeates at a constant rate through the membrane into a confined stream of propane gas or a natural mixed gas. Very small amounts of mercaptan vapors which permeate through the membrane while the latter is in direct contact with the liquid compound suffice to impart the desired odor to the gas, thus permitting rapid detection of leaks in a gas pipe.

However, the membranes recommended by Klass et al do not permit a satisfactory permeation by vapors of perfume (i.e. a mixture of essential oils) when in contact with the dry liquid perfume.

Moreover, in U.S. patent 3,815,828 of Engel, it has been recommended to use a liquid-impervious membrane of a water-insoluble vinyl polymer or copolymer, water-insoluble polymethane or the like in contact with an aqueous emulsion of volatile matter, especially an odoriferous material formed with the help of a surfactant. Vapors of the odoriferous material will permeate the membrane and are gradually released into the surrounding atmosphere as a dry gas, over a period of time which is greater than the time required for an equal amount of the odoriferous material to volatilize in its free unconfined state. However, the permeation rate of the odoriferous material through the membrane is often too low and must be enhanced by impregnating the external surface of the membrane with an aqueous emulsion containing a similar or dissimilar volatile matter, and drying the membrane until the external surface is dry to the touch. Of course, this complicates the manufacture of such dispenser systems considerably.

On the other hand, liquid-wick types and the solid air-treating agents, i.e. solid compositions from which volatile air-treating materials slowly vaporize when the solid is exposed to air are predominant among the air-treating systems, and in particular room deodorizers and the like, the sale and manufacture of which has expanded substantially with the result that a large variety of air-treating products or agents have been developed for commercialization. Such air-treating agents, described

for instance in US Patents Nos. 2,691,615 and 2,929,055, comprise a solid gel containing volatile air-treating materials.

Air-treating systems of this type have many advantages; however, while being satisfactory in use in many respects, they generally exhibit a less satisfactory release mode. Thus, their rate of release of active ingredient is initially high, but suffers a rapid decline with the passage of time. Such a pattern of exponential decay is often referred to as "first-order decay". As a result, the amount of released agent may initially exceed the amount required for effective air treatment, while at some later time it may be inadequate for the task. Furthermore, the release rates of such systems will be affected by temperature and humidity changes, thereby introducing additional variables that must be considered by the manufacturer. In addition, fractionation of the components of a perfume consisting of essential oils is seen to occur, thereby further increasing the possibility of erratic release patterns. Thus, the pleasant fragrance that may initially be present will vary and disappear with the passage of time and with the resultant change in concentration of the various essential oil components. Correspondingly, the effective odor counteraction that may be achieved initially will also vary and diminish with time. These effects are seen to occur as the concentration of the lower boiling components diminishes in favor of that of the higher boiling components.

Various systems which are seen to exhibit such "first-order" decay are disclosed in US Patents 3,016,199; 3,400,890; 3,596,833; 3,567,118; 2,481,296; and 3,578,545.

The element common to each of these systems is that the active ingredient is homogeneously dispersed or dissolved through the basic matrix. This matrix can be as thin as a membrane (3,567,118) or as thick as a chunk of gel. The kinetics of release from such a matrix depend greatly on the geometry and loading of the system. As noted above, these systems exhibit exponential decay of release rate with respect to time. Gradually diminishing and varying odorant level and odor counteraction are observed rather than the desired constant, uniform, controlled release of fragrance.

Moreover, all of the known systems giving off dry fragrance vapors suffer from the drawbacks that it is difficult to determine at which point in time the system is exhausted, and there is left a container filled with an undesirable liquid residue the disposal of which presents problems.

Also, it will easily occur that a dispenser is discarded while still retaining in its liquid filling a considerable amount of expensive essence or the like odoriferous air-treating agent.

It is, therefore, a main object of this invention to provide a system for delivery of essential oil-type air-treating agents which provides a substantially uniform, controlled release of said agents to the atmosphere, i.e. a "Zero order" release.

It is still a further object to provide a system which substantially minimizes fractionation among the components of the essential oil type air-treating agents as well as between the water and essential oil ingredients.

It is yet another, preferred object of the invention to provide a system of the type described which makes it easy to detect exhaustion of the air-treating agent therein, thereby avoiding waste of expensive agent.

It is finally an object of the invention to provide a system of the type described which is easily disposed of, being emptied of all liquid contents.

These objects are attained, according to the invention, in a dispensing system as initially described which is characterized in that, in combination

(a) the odor-controlling agent is an essential oil type air-treating agent in the reservoir;

(b) the membrane is a hydrophilic membrane mechanically resistant to water up to 60°C and having an equilibrium water content of at least 15 % by weight calculated on the total weight of the membrane; and

(c) the liquid is an aqueous dispersion of the air-treating agent defined under (a) ⁱⁿ an aqueous dispersion medium.

Preferably, the walls of the reservoir other than the portion thereof constituted by the membrane are collapsible, and the liquid thus fills the reservoir at all times until consumption is complete. According to another embodiment, the walls of the reservoir are constituted by the membrane and are collapsible.

The operation of the membrane involves selective sorption of air-treating agent and water into the membrane at the internal surface of the latter, selective diffusion or flow through the membrane and then desorption of vapors from the external membrane surface into the air.

By using a hydrophilic membrane as part of the reservoir wall, constant release of the aqueous-based air-treating agent is attained. The presence of the water in the liquid phase is essential in that it plasticizes the membrane and lowers the glass transition temperature of the membrane material so that the diffusive transport rate of the perfume through the membrane can be of practical value in freshening the air in a closed room. The hydrophilic membrane as defined meters the transport of aqueous-based perfume from the enclosed reservoir at a constant rate for a prolonged and controllable period of time. This is in contrast to the commercially available known systems which, as previously noted, exhibit a gradually diminishing level of active ingredient. Furthermore, the kinetics of release do not depend on the geometry and loading of the system. Rather, the total period of release depends solely on the size of the reservoir.

In addition, the controlled release of aqueous-based air-treating agent by the use of a hydrophilic membrane causes only a negligible amount of fractionation of the essential oil components of the perfume present. Thus, contrary to conventional wick systems, for example, which exhibit fast release of the low boiling components followed by the components boiling at medium and high

temperature ranges, the instant systems exhibit similar percentage releases for all three portions through the swollen hydrophilic membrane. As a result, there is a uniformity of fragrance throughout the entire period of activity of the dispenser. The initial, desired fragrance is substantially maintained without the variations that would result from component fractionation. Likewise, the desired and expected level of odor counteraction is maintained without the diminution thereof resulting from component fractionation.

It is also possible to reduce or eliminate completely fractionation between the water and the essential oil type agent as a result of proper formulation of the system. Thus, undesirable release modes wherein only a portion of the essential oil is released before the water content is depleted or wherein the essential oils release and deplete faster than water are avoided. Accordingly, the unnecessary waste of essential oil and possible insufficient release rate of the first of these modes as well as the initially higher than required release and subsequent diminished fragrance level of the second mode are substantially eliminated. The instant system thus establishes that the release rates of the water and essential oil are proportional to their weight fractions by a similar constant so as to avoid the undesirable release patterns described hereinabove.

In the dispenser system according to the invention, rigid containers wherein the membrane represents one side thereof as well as collapsible containers can be used. The containers are preferably fitted with means for vacuum relief.

All conventional volatile odorous air-treating agents of the essential oil type, in particular perfumes, are applicable for use in the instant systems. A wide variety of such materials are known to those skilled in the perfuming arts. They may comprise one or more natural materials or synthetic aromatic agents or mixtures of the two.

Such essential oil-type air-treating agents are primarily perfumes of which a representative selection is given in British patent specification 1,336,495 of CIBA-GEIGY AG, Basel, Switzerland, on page 5, lines 92 to 106 and in British patent specification 1,517,410 to S.C. Johnson & Son, Inc. Racine, Wisconsin in Table I on page 5 (see also French patent application 2,336,946, published September 2, 1977).

Furthermore, these agents comprise synthetic "perfumes" being mixtures of a base and a head note selected from the deodorants and reodorants listed in British patent specification 1,432,163 of CIBA-GEIGY AG beginning in line 39 of page 3 and ending in line 29 on page 6; similar compositions are also described in German patent 1,617,018 of Rudolf RANDEBROCK, Garstedt, Germany.

The essential oil-type air-treating agent must be dispersed in an aqueous dispersion medium in the form of a solution or emulsion or simultaneously part of its components dissolved and the remaining components emulsified. The aqueous dispersion medium can be water or a water-solvent mixture of water with alcohols, glycols, ketones, aldehydes, and the like, e.g. water-ethanol, water-glycerol, water-ethylene glycol, water-

cellosolve, water-acetone, water-acetaldehyde, and the like. An emulsion of hydrophobic essential oil in water or the aforesaid water-solvent mixtures can be formed utilizing an appropriate emulsion system. Various optional ingredients may also be included such as surfactants, thickeners, dyes, stabilizers, and the like. The concentration of the air-treating agent may be selected in accordance with the particular needs with regard to intensity and duration of fragrance, and the like.

Preferably, the aqueous dispersion contains, per 100 parts by weight thereof, from 0.5 to 25 parts by weight of the air-treating agent and correspondingly from about 95 to 45 parts by weight of water or a liquid water/organic solvent mixture.

Especially preferred are dispenser systems according to the invention in which the air-treating agent is an essence, in particular a floral or herbal or wood essence, and in particular those systems in which the essence is present in an amount of from 0.5 to 5 parts by weight, and correspondingly the aqueous dispersion medium is present in an amount of about 97 to 80 parts by weight, in every 100 parts by weight of the aqueous dispersion.

The hydrophilic membrane is selected so as to exhibit good mechanical strength and, most importantly, a minimum equilibrium water content of 15%, and preferably above about 30%. Such values are required in order to maintain effective essential oil permeability. Applicable hydrophilic membranes include cellophane; Cuprophan (cellulosic membrane prepared by cuprammonium process); high molecular weight, at least 98% to fully hydrolyzed polyvinyl alcohol (e.g. manufactured by Mono-Sol Division

of Chris-Craft Industries, Inc.); crosslinked polyvinyl alcohol; hydrogels; hydrophilic groups-containing polyvinyl chloride with inert absorptive filler (e.g. manufactured by Amerace Corp., Butler, N.J.); cellulose triacetate; copolyether polycarbonate; polyethylene glycol-polyethylene terephthalate block copolymer, [see Lyman et al, Biochemistry 3, 985(1964)]; hydrophilic polyurethane (see U.S. Patent 3,822,238); and the like.

Applicable hydrogels are disclosed in numerous references including US Patents 3,520,949, 3,632,416, 3,641,237, 3,721,657, 3,784,540, 3,929,741, 3,947,401, and others. Such hydrogels are polymers of monomers containing at least one hydrophilic group which polymers have been crosslinked with a polyunsaturated crosslinking agent. Such hydrophilic monomers include hydroxyalkyl acrylates and methacrylates, diacetone acrylamide, acrylamide, methacrylamide, acrylamido propane sulfonic acid, 2-(alkoxy) ethyl acrylates and methacrylates, alkyl aminoalkyl methacrylates, ethylenically unsaturated carboxylic acids, vinyl pyrrolidone, diethylene glycol monoacrylate, diethylene glycol monomethacrylate, glyceryl methacrylate, pentaerythritol methacrylate, and the like. Typical crosslinking agents are vinylic, vinylidene or allylic in nature and include polyunsaturated polyesters formed between a polyhydroxy alcohol and an ethylenically unsaturated carboxylic acid, aliphatic polyvinyl monomers, aromatic polyvinyl monomer, polyalkyl monomers, allyl-vinyl monomers, methacrylic acid anhydride, alpha, omega-diamino acrylamides, and the like. The aforementioned monomers are only exemplary of the large number and variety of hydrogel components known to those skilled in the art which can be utilized in the instant invention.

In addition, the hydrophilic membranes can be further supported by macroporous materials such as woven and non-woven fabrics, filter paper, cardboard or macroporous plastic materials such as a porous polyvinyl chloride sheet, a porous polypropylene sheet, and the like. In general, any macroporous sheet which does not affect the release kinetics of the hydrophilic membrane system can be used.

Preferred membranes have an equilibrium water content of 30% or higher. The thickness of the membrane preferably ranges from 0.005 to 0.05 cm. The membrane should preferably show from 120 to 200 % and in most preferred cases from 140 to 180 % swelling in contact with water at room temperature.

With regard to the rate of release, the desired constant rate can be controlled by the type of hydrophilic membrane selected and the membrane thickness and surface area. The total period of release will be determined by the amount of aqueous-based air-treating agent. Due to the difference in permeation rate of water and essential oils through any specific water-swollen hydrophilic membrane, it is necessary in the design of a particular unit to consider the amount of essential oil that would be released in vapor form as long as the membrane is in a water-swollen state. This determination would yield an optimum composition of essential oil in water and thereby eliminate undesired waste or deficiency of active ingredient.

The container adopted to contain the instant system can be, for instance, a rigid container wherein the membrane serves as one of the walls. The membrane can be supported in any convenient manner. The container should

desirably be fitted with means for vacuum relief so as to avoid the formation of a partial vacuum with the passage of time, such means including pinholes, one-way valves, capillary tubes and the like. The container can also be prepared in soft, collapsible form such as a plastic bellow or a plastic packet or envelope. The collapsible construction removes the necessity for including vacuum relief means.

Although the previous discussion has made primary reference to essences as the air-treating material, it should be noted that the instant invention is equally applicable to the dispensing of disinfectants, insecticides, respiratory medicines, and the like, especially in mixture with an essence.

The following examples will further illustrate the embodiment of the invention. In these examples, all parts and percentages given are by weight unless otherwise noted.

The essence used in these examples has a minty herbal fragrance. The preservative used in Examples I to V consisted of 65 % methyl-paraben and 35 % propyl-paraben.

As emulsifiers there were used

- (X) octylphenolpolyethylene oxide (Triton X 100)
- (Y) triethanolamine laurylsulfate (Maprofix TLS 500)
- and
- (Z) phosphatide (Alcolec 329) in the weight ratios stated in each example.

Example I

This example illustrates a typical system of the instant invention.

For purposes of this example, the following hydrophilic membranes were utilized:

	Membrane	Thick- ness (Mils)	Degree of Swelling (%)	Equili- brium Water Content (%)
1	Hydroxyethylmethacrylate hydrogel	6.8	35.6	26.3
2	Hydroxyethylmethacrylate hydrogel	8.0	35.6	26.3
3	Cellophane	3.0	117.2	53.95

(1 mil \approx 0.0025 cm)

in conjunction with the following aqueous-based air-treating material

	<u>Parts</u>	
Water	95.0	
Essence	1.0	
Surfactant	1.5	(X:Y:Z =
Color (green dye)	0.1	0.7:0.6:0.2 parts)
Preservative	0.1	
Cellosolve-acetaldehyde blend (1:1 parts)	2.3	

The fragrance release studies were conducted in a membrane cell designed with a small capillary connected

to the atmosphere in order to prevent the formation of a partial vacuum due to release of the air-treating material. Pre-swollen membranes were mounted on the cell and the liquid introduced thereafter. The cell was inverted to bring the liquid into contact with the membrane. The loaded cells were then enclosed in a chamber where air was blown through at a predetermined rate. The temperature was maintained at 26°C and the humidity at 71%. The release rate was determined gravimetrically for a period of time up to about 220 hours, i.e. prior to a complete depletion of the reservoir. As a control, an open cup of air treating material was subjected to the same atmospheric conditions.

The following results were obtained:

	Air Flow Rate (l/min.)	Release Rate (10^{-3} g/cm ² hr.)
Open Cup	$< 3 \times 10^{-3}$	6.154**
Membrane # 1	$< 3 \times 10^{-3}$	4.118
Membrane # 2 *	$< 3 \times 10^{-3}$	2.927
Open Cup	10	12.50 **
Membrane # 1	10	4.634
Membrane # 2 *	10	4.146
Membrane # 3	10	7.5

* Test conducted in completely sealed cell.

** Initial Rate.

The above noted results clearly illustrate the desired reduction in initial release rate exhibited by the systems of this invention. Furthermore, the results indicate that the fragrance release through the instant membrane devices is "zero-order" in contrast to the open

cup evaporation which exhibits "zero-order" release only during the initial stage.

The latter result is depicted graphically in Fig. 1 which presents a plot of release (gm/cm^2) versus time (hours) at an air flow rate of 10 litre/min. Thus, it is seen in Fig. 1 that the systems as reflected in membranes 1-3 provide a substantially controlled, constant rate of release as contrasted with the open cup which exhibits a significantly decreased release with the passage of time.

Example II

The procedure of Example I was repeated utilizing the identical aqueous air-treating material and conducting the test procedure at 26°C . and at an average humidity of 59%. Each membrane was tested for at least 200 hours, with several being tested up to 400 hours.

The following tables describe the tested membranes and the test results obtained therewith.

#	Membrane	Thickness (mils)	Degree of Swelling (%)	Equili- brium H ₂ O content (%)
4	Crosslinked block polymer of 60% 2-hydroxy-ethylmetha- crylate (A) and 40% iso- cyanate-terminated polyether-bisurethane (B) (HEMAC)	10.0	20	16.67
5	UV cured 70 (A):30 (B) HEMAC	3.5	21	17.36
6	80 (A) : 20 (B) HEMAC	10.0	37	27.00

	Air Flow Rate (l/min.)	Release Rate (10 ⁻³ g/cm ² hr)
Open Cup	> 12	20.7
Membrane # 4	> 12	1.449
Membrane # 5	> 12	4.000
Membrane # 6	> 12	6.418

Once again the desired reduction in initial release rate and the release through the membranes in a "zero-order" mechanism were noted. Graphical depictions of the performances of membranes 4-6 are presented in Fig. 2.

Example III

A sealed container was prepared whereby a filter paper dip coated with hydroxyethyl-methacrylate monomer was then cured with ultra-violet radiation directly onto the inside of a front perforated panel, the resulting membrane having a thickness of about 10 mils (about 0.025 cm) and an effective area of 12.932 cm^2 . The aqueous air-treating material of Example I was then introduced into the container by syringe and the pinhole sealed. Release measurements were conducted at room temperature and a humidity of 61% and with substantially no air flow. The unit was run for a period of 44 days and was found to exhibit a constant release rate of $0.1089 \text{ g/cm}^2\text{day}$ and a total release of 1.4082 g/day . A graph of the release rate, noted as Fig. 3, revealed a "zero-order" release mechanism.

Example IV

The testing apparatus, procedure and aqueous air-treating material of Example I were utilized herein in connection with a microporous polyvinylchloride film (# 7) containing an inert, absorptive, inorganic filler, said membrane having a 20 mil thickness, a 150% degree of swelling and a 60% equilibrium water content. The release rate, as determined over a period of 65 hours at room temperature, 61% humidity and in the absence of air flow, was found to be $0.39 \text{ g/cm}^2\text{day}$. A plot of the individual readings revealed a "zero-order" release mechanism.

Example V

The test procedure of Example I was repeated utilizing the following aqueous air-treating materials and hydrophilic membranes.

	<u>Water Content (parts)</u>	<u>Essence Content (parts)</u>	<u>Other Ingredients (parts)</u>
B	96	0.85	3.15 surfactant, color and preservatives
C	96	0.85	3.15 surfactant + cellu- losic thickener
D	49.5	25.0	25.5 surfactant + non- volatile thickener

(Parts are by weight)

#	Membrane	Thickness (mils)	Degree of Swelling (%)	Equili- brium Water content (%)
8	Cuprophon 150 PM	0.984	116.5	53.8
9	Cuprophon 250 PM	1.5	115.0	53.5
10	Water-insoluble poly- vinyl alcohol (cold H ₂ O insoluble)	2.6	140.0	58.3

Each test was conducted at two temperatures, at an average humidity of 43% and with an air flow in excess of 12 l/min. Open cup controls were also included in the test procedure.

The results of these tests are presented in the following table.

<u>Membrane #</u>	<u>Air Treating Agent</u>	<u>Temp. (°C.)</u>	<u>Release Rate (gm/cm² day)</u>
8	B	23.3	1.1520
8	B	35.0	3.0648
8	C	23.3	1.0047
8	C	35.0	2.3460
8	D	35.0	0.7093
9	B	23.3	1.3440
9	B	35.0	2.8464
10	B	23.3	1.260
10	B	35.0	2.3520
10	C	23.3	0.9874
10	C	35.0	2.3977
10	D	35.0	0.5578
7	C	35.0	1.9583
3	B	35.0	2.6136
Open Cup	B	23.3	1.8240
Open Cup	B	35.0	3.1872
Open Cup	C	23.3	1.9533
Open Cup	C	35.0	3.4622

Once again, the release data for these systems revealed a "zero-order" release rate up to about 80-90% of the total release capacity.

Example VI

This example illustrates a further advantage of the instant system in terms of reduced fractionation effects:

Initially, fractionation effects between essential oil components of an essence of "natural" fragrance (wood, herbal or floral) were determined. In this instance, a preswollen membrane of water-insoluble polyvinyl alcohol obtained by 99% hydrolyzation of polyvinylacetate (degree of swelling 140%, equilibrium water content 58.3%, wet thickness 2.6 mils, insoluble in water below 60°C) was mounted on a closed cell and the liquid content introduced thereon. The liquid content was stirred and air at a controlled rate (>11 liter/min for membrane cell and

>5 liter/min for open cup) was blown across the membrane surface to accelerate release. The time course of release was followed gravimetrically. Periodic samples were taken of the liquid remaining in the cell and analyzed by gas-liquid chromatography. Comparable analyses were conducted on liquid introduced into an open cup. The essential oil components were categorized as low (0-15 minute retention time), medium (16-34 minute retention time) and high (35-44 minutes retention time).

The polyvinylalcohol had a viscosity of 11.3 centipoises at 60°C (concentrate in water), and the same aqueous solution had viscosity of 27.5 centipoises at 25°C.

The following formulations were utilized:

	<u>Parts</u>	
	<u>E</u>	<u>F</u>
Essence	0.85	2.55
Surfactant	1.34	4.02
Dye	0.50	0.50
Preservative	1.36	4.08
Glycerin	-	1.50
Demineralized water	95.95	87.35

(in E: X:Y:Z = 68:55:11; in F: X:Y:Z = 204:165:33)

The preservative consisted of methyl-paraben 0.906, propyl-paraben 0.302, and cellosolve 0.906 parts in Example VI-E and of methyl-paraben 0.906, propyl-paraben 0.456 and cellosolve 2.718 parts in Example VI-F.

The GLC values are presented in the following tables (GLC = gas liquid chromatography).

Upon combining the results of total release by weight loss as well as the amount released per unit area for the essential oil components, the percentage essential oil released as well as the percentage released for the essential oil components is determined and are also presented in the following tables. In each instance, the open cup area was 5.1875 cm^2 and the membrane area was 23.7583 cm^2 .

Formulation E

Time (hr)	GLC Analysis			Control (open cup)			% Oil Release
	Low (%)	Med (%)	High (%)	Low (%)	Med (%)	High (%)	
0	17.9	71.4	10.6	0	0	0	0
3.92	17.6	71.2	11.0	9.59	8.29	4.55	8.05
23.42	15.5	69.9	14.6	37.12	28.89	--	27.39
48.75	9.9	68.9	21.2	75.03	56.44	9.69	54.87
71.67	5.8	67.1	27.1	89.95	70.89	20.79	69.43
95.26	3.4	67.0	29.6	95.34	76.97	31.48	75.46

Membrane Cell

Time (hr)	GLC Analysis			% Release (per cm ²)			% Oil Release
	Low (%)	Med (%)	High (%)	Low (%)	Med (%)	High (%)	
0	17.9	71.4	10.6	0	0	0	0
4.97	18.1	71.3	10.5	2.46	3.66	4.37	3.52
24.7	18.4	70.8	10.8	2.90	6.31	3.70	5.52
49.92	19.5	69.1	11.4	6.43	16.88	7.62	14.11
74.42	19.2	69.5	11.3	12.81	20.85	13.27	18.69
97.85	20.2	71.1	8.7	13.04	22.49	36.12	22.15

Formulation F

Time (hr)	GLC Analysis			Control (open cup)			% Oil Release*
	Low(%)	Med (%)	High (%)	Low(%)	Med(%)	High(%)	
0	19.81	71.15	9.03	0	0	0	0
2.67	19.43	71.13	9.44	6.19	4.35	0.18	4.32
22.7	15.09	73.43	11.48	46.01	26.89	10.05	29.16
47.67	0.20	85.76	14.23	99.54	45.24	28.40	54.57
70.92	0.20	85.00	14.80	99.60	52.10	34.39	59.91

Membrane Cell

Time (Hr)	GLC Analysis		High (%)		% Release* (per cm ²)			% Oil Release***
	Low (%)	Med (%)	Low (%)	Med (%)	High (%)	Med (%)	High (%)	
0	19.81	71.15	9.03	0	0	0	0	0
3.85	20.29	69.91	9.80	6.16	9.97	0.33	8.38	8.38
24.0	20.95	70.38	8.67	13.77	19.34	15.82	18.47	18.47
49.09	22.37	68.61	9.01	44.81	52.87	51.30	51.13	51.13
73.29	24.71	65.25	10.04	80.60	85.73	82.72	84.44	84.44

* Data depicted in Fig. 4.
 ** Data depicted in Fig. 5.
 *** Data depicted in Fig. 6
 **** Data depicted in Fig. 7

The data presented hereinabove thus clearly reveal the substantial reduction in essential oil and essential oil-water fractionation with the instant system. Referring specifically to the graphs (Figs. 4-7) for formulation F, linear release characteristics are exhibited. The percentage essential oil vapor release follows closely with the percentage total release (Fig. 6) indicating there is no fractionation between water and essential oil as compared to the open cup evaporation where fractionation does occur (Fig. 7). In other words, the essential oil concentration in the polyvinyl alcohol membrane system remained pretty much the same during the whole course of release study. Figures 4 and 5 further show that there is practically no fractionation among components of the essential oil in the PVA membrane system as compared to that in the open cup control where fractionation prevails.

Corresponding data were developed for formulation F utilizing the identical test procedure except for the elimination of the air blown across the membrane surface. Thus, stagnant conditions were achieved. The following results were obtained.

Time (hr)	<u>Membrane Cell</u> GLC Analysis			<u>Membrane Cell</u> (% Release)			% Oil Release
	Low(%)	Med(%)	High(%)	Low(%)	Med(%)	High(%)	
0	29.50	56.97	13.53	0	0	0	0
76.50	35.84	48.90	15.26	--	--	--	7.60
167.67	34.64	50.54	14.81	15.6	36.3	21.4	28.16
243.75	32.80	55.74	11.47	56.2	61.5	45.5	60.64
313.84	43.39	39.73	16.97	66.8	78.2	60.9	68.81

It is seen that comparable elimination of fractionation is also achieved under stagnant conditions.

Furthermore, only minimal fractionation was also observed when evergreen oil and honeysuckle oil, absent surfactant concentrations, were subjected to similar test procedures.

The membranes usable in the dispensing system according to the invention must be mechanically resistant to water up to 60°C, i.e. they should swell, but should not melt or be otherwise destroyed when in contact with the aqueous dispersion of air-treating agent below that temperature.

Summarizing, it is seen that this invention provides a unique system for the controlled release of air-treating materials. Variations may be made in proportions, procedures and materials without departing from the scope of the invention as defined by the following claims.

In particular, the system according to the invention permits easy detection of the exhaustion of the system by the fact that the reservoir is empty.

Moreover, the empty reservoir can be more easily destroyed than the known systems still containing a large proportion of the liquid filling in their interior even after exhaustion of the air-treating agent.

Preferred embodiments of the dispenser system according to the invention shall now be described in detail. These embodiments are illustrated in the accompanying drawings, in which

Fig. 8 shows in lateral view a preferred embodiment of the dispenser system;

Fig. 9 shows a bottom view of the embodiment of Fig. 8;

Fig. 10 is a sectional view of the same embodiment taken in a plane indicated by X - X in Fig. 9;

Fig. 11 is a lateral view of another embodiment of the dispenser system;

Fig. 12 is a bottom view of the embodiment shown in Fig. 11 and;

Fig. 13 is a sectional view of the embodiment of figures 11 and 12 taken in a plane indicated by XIII - XIII in Fig. 12.

The embodiment shown in figures 8 to 10 comprises a frustospherical hull 1 the open base of which has curved cutaway wall portions 2 between which four foot portions 3 are left on which the hull can be placed upright on a shelf or the like horizontal support. In a central plane above which the hull portion constitutes a hemisphere, a perforated plate 4 or the like grid is fastened, e.g. by thermo-welding a circumferential margin 5 thereof on the inside surface of the hemispherical portion of hull 1.

In the hemispherical space 6 enclosed between plate 4 and the dome of hull 1 thereabove, there is lodged a hydrophilic membrane 6 filled with an air-freshening liquid 7. Arrows A indicates air flowing through the windows formed by cutaway wall portions 2 of hull 1 and taking up

vapors of air-freshening agent and water that have permeated the membrane 6.

In the embodiment of Figures 11 to 13, the frustoconical hull 10 consists of an upper hemispherical half 11 as dome part and a lower frustospherical segment as base part 12. The lower annular rim portion 11a of the open end of dome part 11 bears an inner circumferential sleeve portion 13 of smaller diameter than the inner width of the upper end 14 of base part 12, whereby a shoulder 15 is formed externally about sleeve portion 13 which shoulder 15 comes to rest on the rim surface of upper end 14. Sleeve portion 13 and upper base part end 14 can be permanently fastened together by thermo-welding or gluing after the internal parts housed in the interior of hull 10 have been assembled.

The base part 12 is provided with a plurality of cut-in wall portions downward from its upper end 14 and forming windows 16 in the assembled hull 10 which permit the passage of air therethrough during use. The bottom end of base part 12 has a central opening 17 and about the latter a circumferential inner shoulder 18 is provided on the inner wall of base part 12. A slotted grid 20 or the like plate is seated by means of feet 21 on the shoulder 18 and bears an axial upwardly directed peripheral flange 22 which surrounds a hydrophilic membrane 23 placed on the grid 20 and held in place thereon by a cylindrical sleeve 24 which depends from the upper inner region of the wall of dome part 11 and is preferably integral with the latter. The lower end of sleeve 24 fits snugly into peripheral flange 22 of grid 20 and urges the periphery of membrane 23 against grid 20.

At the top of dome part 11 there is provided a vacuum relief means which, in the embodiment shown, is a slit rubber plug 25 which admits air from the outside whenever a vacuum develops in the interior 26 of sleeve 24 due to diffusion of air-freshening agent and water through the membrane and evaporation of these components from the external (lower) face of membrane 23 and escape of the vapors via slots 27 of grid 20 and windows 16.

Air-freshening liquid can be filled into the sleeve interior 26 after the membrane 23 has been secured liquid-tight across the lower end of sleeve 24, with the aid of an injection means introduced through the slit of rubber plug 25.

The rubber plug 25 can also be replaced by a rubber check valve or rubber grommet or the like means of known construction.

As an alternate type of attachment of the membrane 23, the lower end of sleeve 24 can be provided with an external threading and peripheral flange 22 of grid 20 can be provided with an internal threading whereupon the membrane 23 is placed in flange 22 or on the lower open end of sleeve 24 and the latter two parts are then screw-connected together holding the periphery of membrane 23 firmly and liquid-tight between them.

For purposes of storage, the dispenser can be sealed in a vapor-tight envelope (not shown) or the like sealing-in means.

Claims:

1. A dispensing system for vapors of a volatile odor-controlling material comprising a closed reservoir and a membrane forming at least a portion of the wall of said reservoir and having an external surface in contact with the surrounding atmosphere, and an odor-controlling agent-containing liquid in said reservoir in contact with the internal surface of said membrane, characterized in that, in combination,

a) said odor-controlling agent is an essential oil-type air-treating agent in the reservoir;

b) said membrane is a hydrophilic membrane mechanically resistant to water up to 60°C and having an equilibrium water content of at least 15 % by weight calculated on the total weight of the membrane; and

c) said liquid is an aqueous dispersion of said air-treating agent defined under a) in an aqueous dispersion medium.

2. The dispensing system of claim 1, wherein said equilibrium water content is at least about 30 %.

3. The dispensing system of claim 1, wherein the thickness of the membrane ranges from 0.005 to 0.05 cm.

4. The dispensing system of claim 1, wherein the membrane shows from 120 to 200 % of swelling in contact with water at room temperature.

5. The dispensing system of claim 1, wherein said air-treating agent is an essence.

6. The dispensing system of claim 1, wherein said aqueous dispersion contains, per 100 parts by weight thereof from 0.5 to 25 parts by weight of said air-treating agent and correspondingly from about 97 to 45 parts by weight of water or a liquid water/organic solvent mixture.

7. The dispensing system of claim 5, wherein said essence is present in an amount of from 0.5 to 5 parts by weight, and correspondingly the aqueous dispersion medium is present in an amount of from about 97 to 80 parts by weight, in every 100 parts by weight of said aqueous dispersion.

8. The dispensing system of one of claims 1 to 7, wherein said aqueous dispersion is a liquid-water-organic solvent mixture selected from the group consisting of water-alcohol, water-glycol, water-ketone and water-aldehyde.

9. The dispensing system of one of claims 1 to 7, wherein said hydrophilic membrane is selected from the membranes consisting of cellophane; Cuprophan; high molecular weight, fully hydrolyzed polyvinyl alcohol; crosslinked polyvinyl alcohol; hydrogels; polyvinyl chloride containing inert, absorptive filler; cellulose triacetate; copolyether polycarbonate; polyethylene glycol-polyethylene terephthalate copolymer; and hydrophilic polyurethane.

10. The dispensing system of claim 9, wherein said hydrophilic membrane is a membrane of polyvinyl alcohol insoluble in cold water.

11. The dispensing system of claim 9, wherein said hydrophilic membrane consists of hydroxyethyl methacrylate hydrogel having an equilibrium water content of about 25 to 30%.

12. The dispensing system of claim 9, wherein said hydrophilic membrane consists of cellophane having an equilibrium water content of about 50 to 55%.

13. The dispensing system of claim 9, wherein said hydrophilic membrane consists of cross-linked block-polymer of from 60 to 80% by weight of 2-hydroxyethyl methacrylate and correspondingly from 40 to 20% of isocyanate-terminated polyether-bisurethane having an equilibrium water content of from about 15 to 25% by weight.

14. The dispensing system of claim 9, wherein said hydrophilic membrane consists of a filter paper coated with a poly(hydroxyethyl-methacrylate).

15. The dispensing system of claim 9, wherein said hydrophilic membrane consists of a microporous hydrophilic polyvinylchloride film containing an inert absorptive filler and having an equilibrium water content of about 50 to 60% by weight..

16. The dispensing system of one of claims 1 to 7, wherein the walls of said reservoir other than said membrane are collapsible and the said liquid fills said reservoir at all times until complete consumption.

17. The dispensing system of one of claims 1 to 7 wherein the walls of said reservoir are constituted by said membrane and are collapsible.

Fig. 1

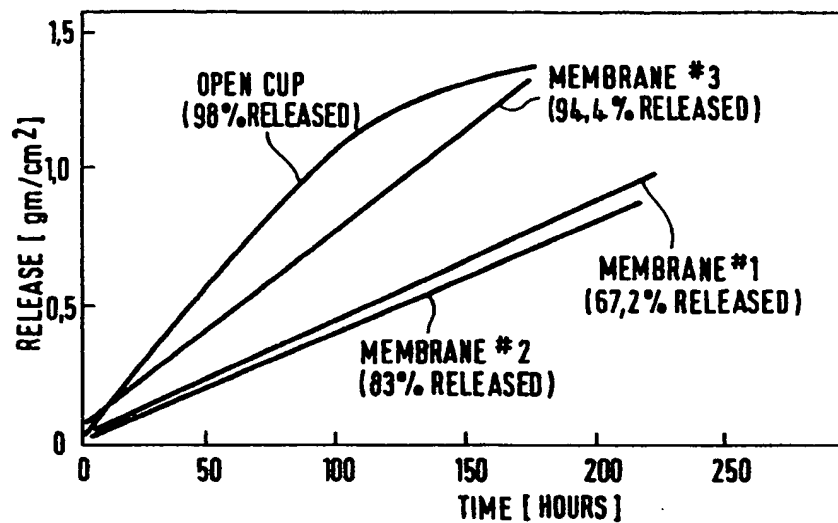


Fig. 2

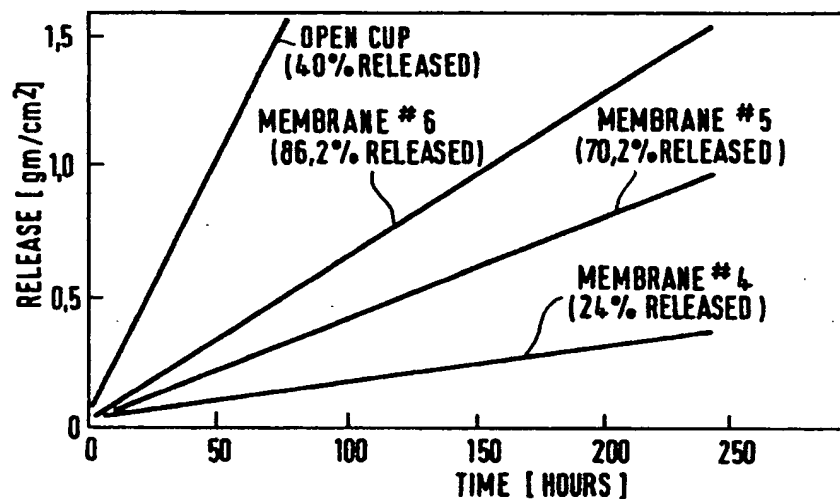
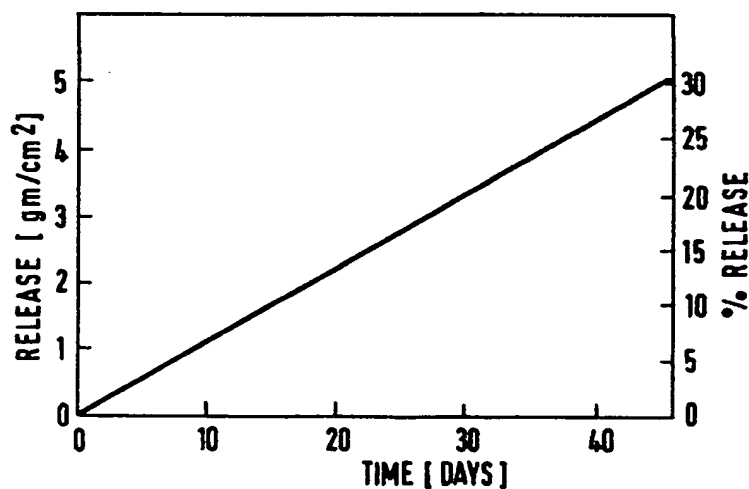


Fig. 3



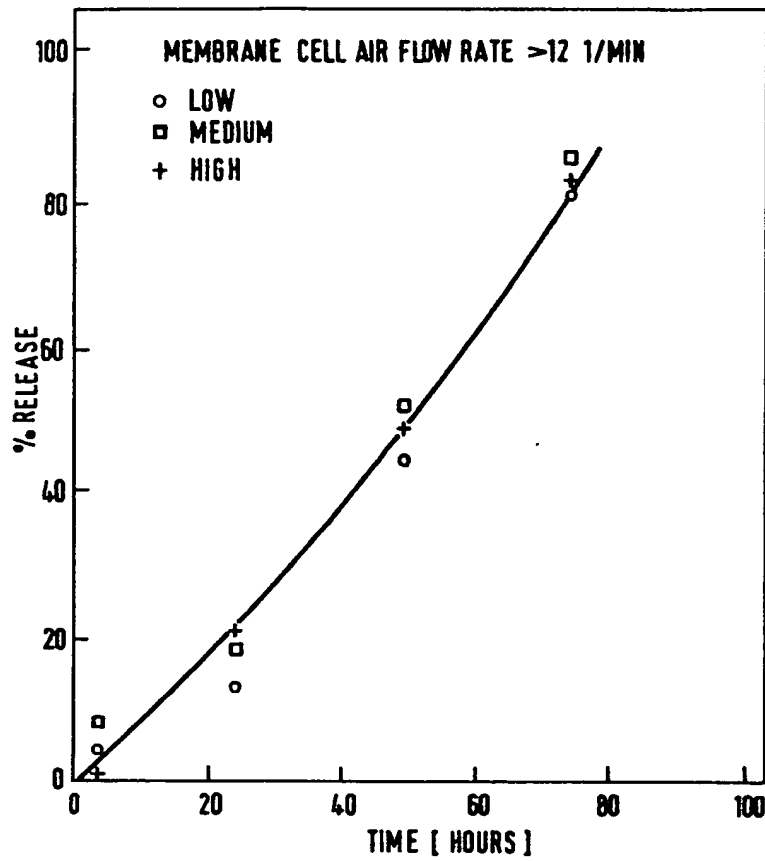


Fig. 4

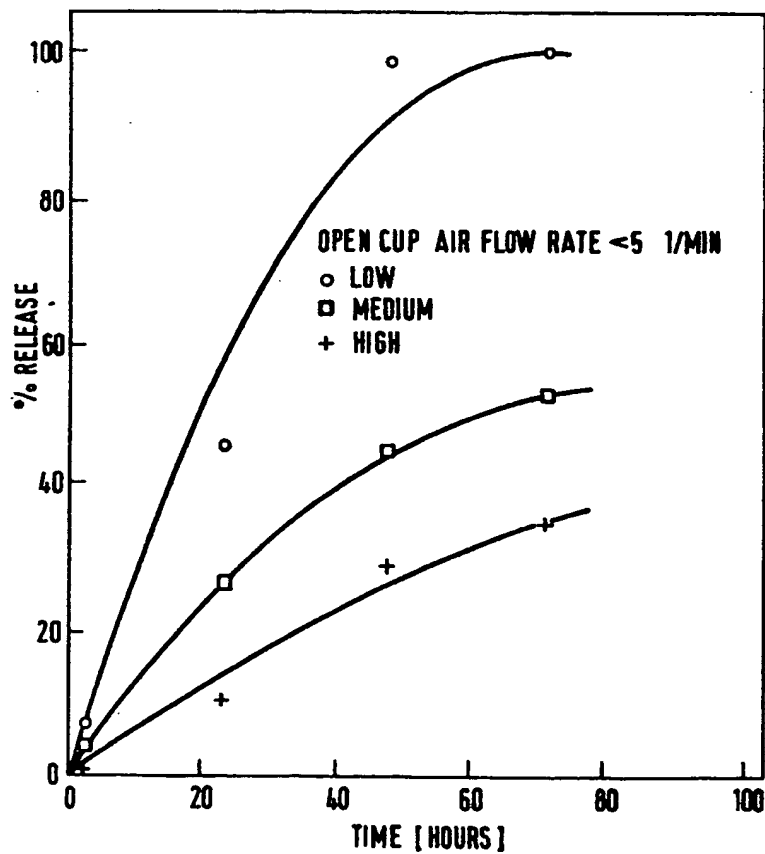


Fig. 5

Fig.6

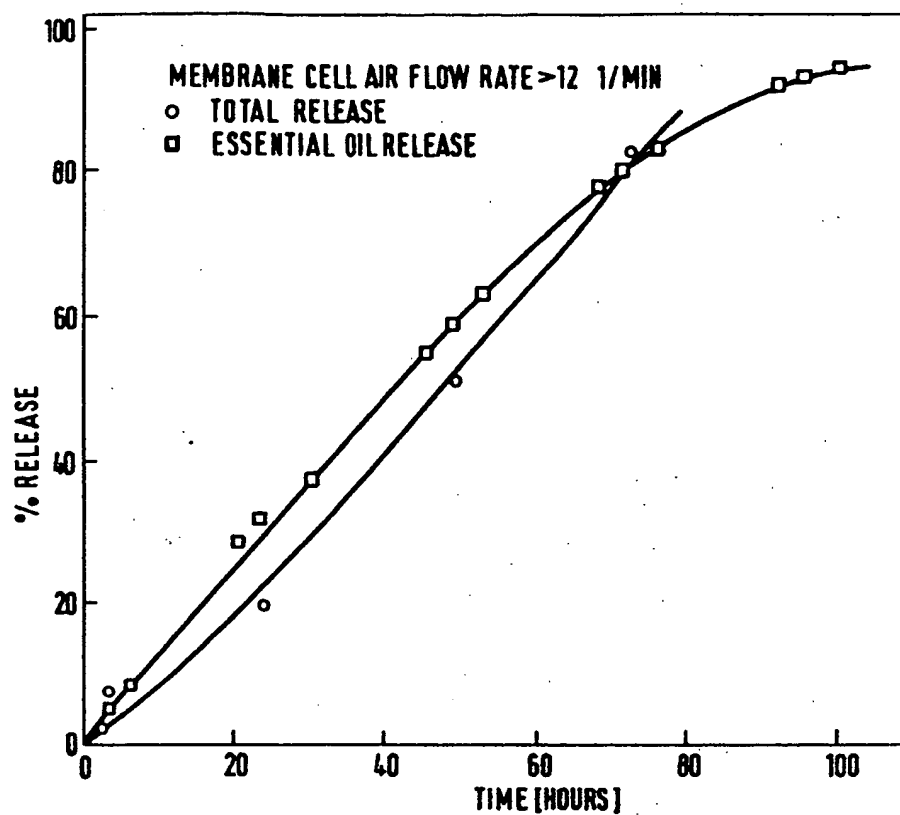


Fig.7

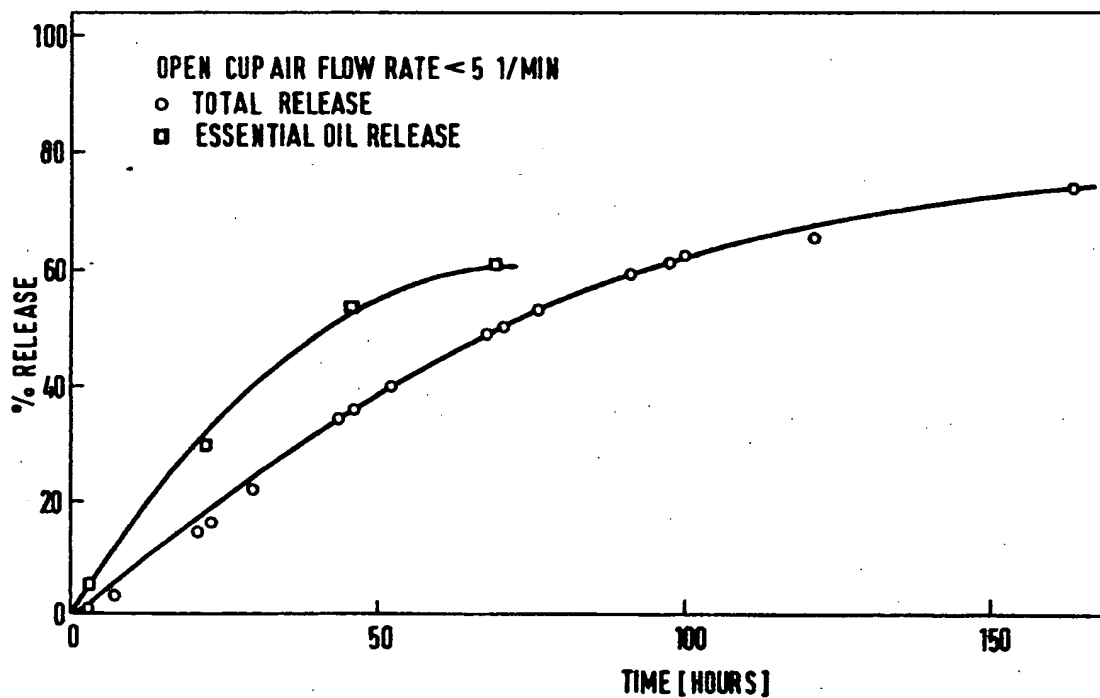


Fig. 8

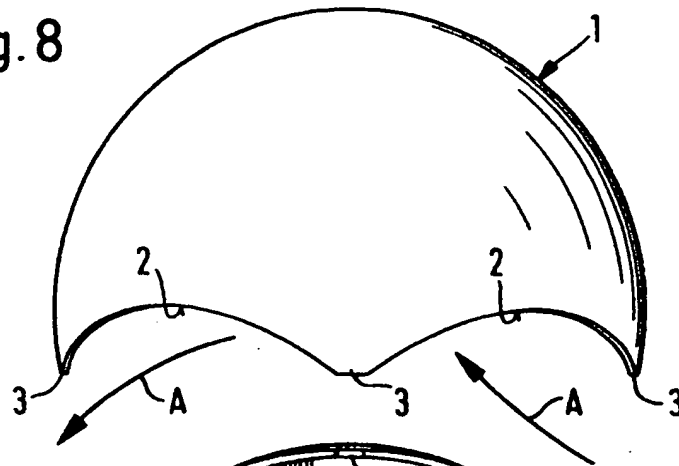


Fig. 9

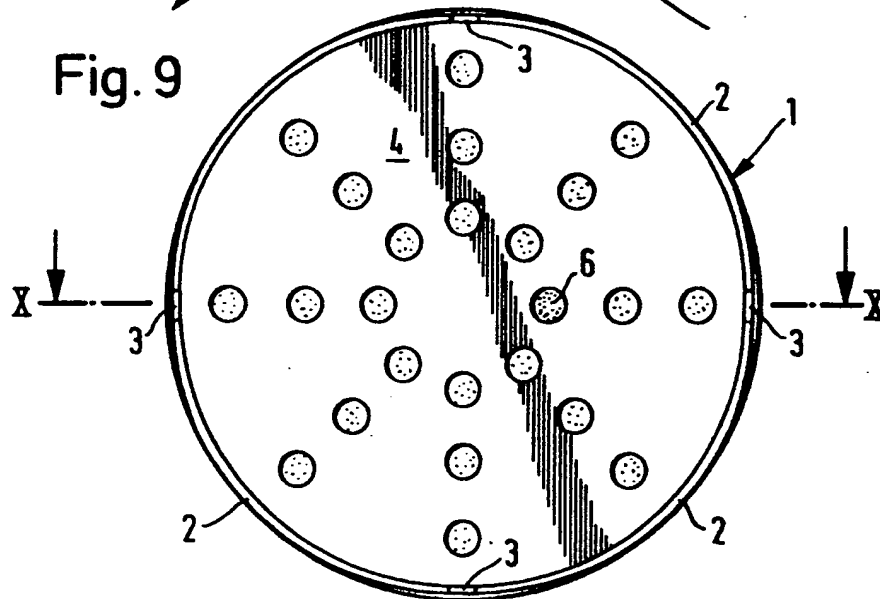


Fig. 10

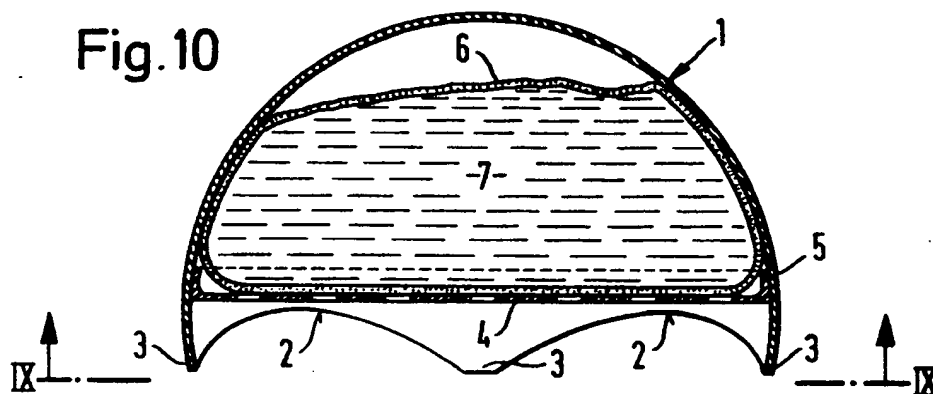


Fig. 11

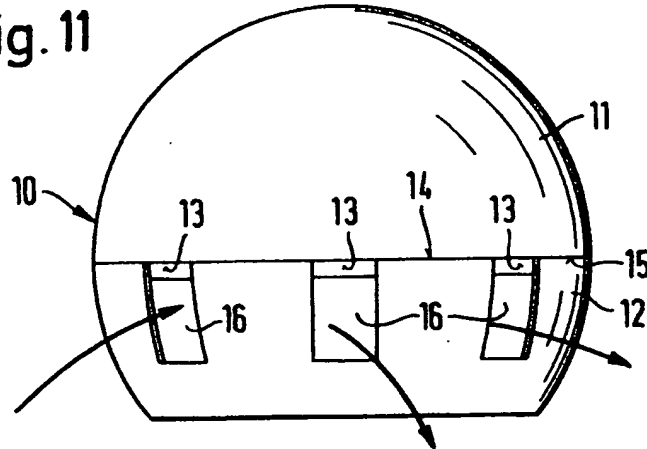


Fig. 12

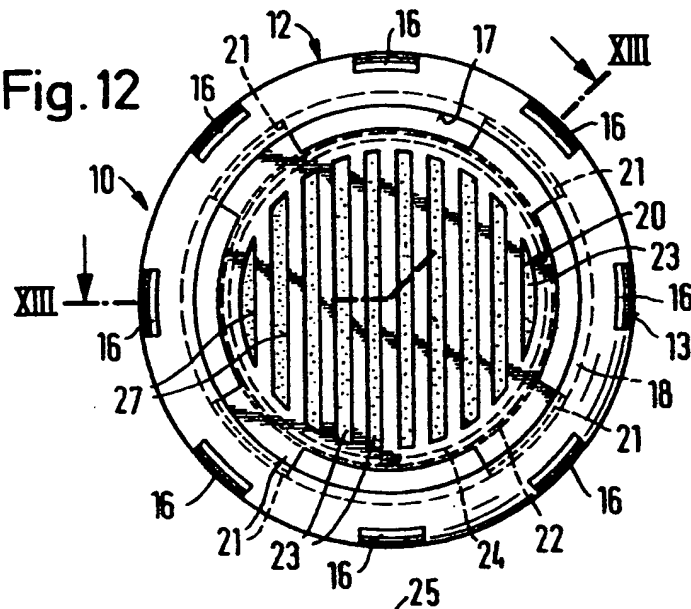
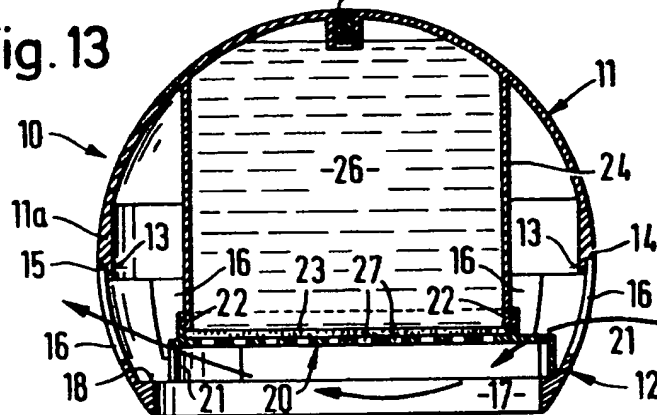


Fig. 13





European Patent
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EUROPEAN SEARCH REPORT

0003003

EP 78 81 0033

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D	<u>US - A - 3 815 828</u> (W.H. ENGEL) * Columns 8,9; claim 1 *	1-17	A 61 L 9/04

A	<u>US - A - 3 578 545</u> (R.M. CARSON) * Columns 5,6; claims 1-8 *	1-17	

A	<u>US - A - 3 688 985</u> (W.H. ENGEL) * Column 8, claims 1,2 *	1-17	
---			TECHNICAL FIELDS SEARCHED (Int.Cl.)
A	<u>US - A - 3 685 734</u> (W.J. PACIOREK) * Columns 1,2 *	1-17	A 61 L 9/04

A	<u>US - A - 3 567 118</u> (T.H. SHEPHERD) * Columns 9,10; claim 1 *	1-17	

			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 22-03-1979	Examiner PELTRE